The Physico-chemical Properties and Concentrations of Organic Contaminants in Waste Materials Recycled in Agriculture

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Abstract

A research programme has commenced to determine the potential transfer of organic contaminants to the human diet from recycled wastes applied to agricultural land as fertilisers and soil improvers, or used as animal bedding in livestock production. This includes: i) an assessment of the potential transfer of organic contaminants to dairy cattle, and milk, via ingestion of contaminated soil and foliage, or alternatively via incidental ingestion of bedding materials, and ii) an investigation of the potential transfer to agricultural crops via plant uptake. A selection of wastes, representative of the range of materials currently used in agriculture in the UK, were analysed for a suite of priority organic contaminants. In general, contaminants were present at low concentrations. For example, polychlorinated dibenzo-p-dioxins/dibenzofurans, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in biosolids and CLOs were, in most cases, between 5-50 times lower than proposed and implemented European limit values for biosolids or composts applied to agricultural land. Polybrominated dibenzo-p-dioxins/dibenzofurans are not currently considered in risk assessments of dioxins and dioxin-like chemicals, but were detected in the biosolids and compost-like-outputs and there potential contribution to the overall toxic equivalency will be assessed. The research will provide evidence to improve confidence in the use of

waste-derived materials in agriculture and establish guidelines to protect the food chain where necessary.

Key words

Ash, agriculture, biosolids, compost-like-output, food, organic contaminants, recycling, waste

Introduction

Recycling of waste materials is encouraged across Europe to reduce waste sent to landfill or incineration (EC, 2011). Increasingly, recycled materials are used in food production for purposes such as animal bedding or as soil improvers and fertilisers. Biosolids have been applied extensively to agricultural land for decades and the impacts on human health are well researched (Smith, 1996), but emerging contaminants need to be considered. Certain outputs from waste combustion processes (eg meat and bonemeal ash (MBMA), poultry litter ash (PLA) and paper sludge ash (PSA)) also demonstrate agronomic benefit as soil amendments and other materials provide alternative types of animal bedding (eg untreated recycled waste wood (RWW), dried paper sludge (DPS), PSA), and are beneficially used in agriculture as alternatives to

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landfill disposal. The management of municipal, and commercial and industrial solid wastes by mechanical biological treatment is also expanding as a means of waste valorisation and landfill diversion and the stabilised biodegradable output from such processes, described as compost-like-output (CLO), has value as a soil conditioning agent (Carbonell *et al.*, 2011). Whilst land application of CLO is currently not permitted in the UK, it is widely practiced in other countries in Europe and in Australia, and pressure could increase to permit application of high quality biocompost to land in the UK. Ash residuals from combustion processes and CLO can also potentially contain contaminants that could represent a hazard to the human food chain (Amlinger, 2004; Smith and Riddell-Black, 2007).

A UK Food Standards Agency (FSA) funded research programme has commenced with the overall aim of investigating the potential transfer of organic contaminants into food arising from the use of recycled waste in agriculture. The research will provide a quantitative assessment of the potential transfer coefficients of principal and emerging organic contaminants to dairy livestock and milk from: i) recycled wastes (RWW, PSA, DPS) used as bedding in dairy production; ii) biosolids and CLO incorporated into the soil and from direct feed contamination with biosolids; and iii) PLA, MBMA and PSA incorporated into the soil. Additionally, the research will investigate the potential transfer of selected organic contaminants to crops by i) screening contaminant transfers using a plant uptake bioassay under controlled

environmental conditions; ii) assessing uptake by a high lipid containing root crop, also under controlled conditions and representing a worst-case exposure route for the food-chain from land applied organic contaminants; iii) conducting a field trial to investigate transfers to cereal grain.

A range of priority established and emerging organic compounds, which would pose a significant risk to human health if they transferred to food products in significant quantities, are under investigation. Polycyclic aromatic hydrocarbons (PAHs), and polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDDs/Fs), which can arise through incomplete combustion, and polychlorinated biphenyls (PCBs), which were widely used in products such as dielectric fluid and paint until the 1970s, are persistent environmental pollutants that can also occur in waste wood (Smith, 2009a). Polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs), polybrominated biphenyls (PBBs), mixed halogenated dibenzo-*p*-dioxins/dibenzofurans (PXDD/Fs) and mixed halogenated biphenyls (PXBs) are related compounds to PCDDs/Fs and PCBs, but little is currently known about their presence in the environment and risk to human health. Perfluoroalkyl compounds (PFCs) are used in nonstick cookware, stain-resistant textiles, coatings on food packaging, components of fire-fighting foam and in many industrial applications including metal plating, hydraulic fluids and surfactants. These compounds were detected in the biosolids and CLO samples, and are of interest as they have a degree of water solubility (van Asselt *et al*., 2013), and therefore could

potentially be taken up by crops. Polychlorinated napthalenes (PCNs) have dioxin-like properties, and are used in applications such as dielectric fluids, engine oil additives and lubricants (Smith and Riddell-Black, 2007). Plasticisers (phthalates, including di(2-ethylhexyl)phthalate (DEHP)), chlorinated paraffins (plasticizers, flame-retardants, lubricant and paint additives), chlorobenzenes (previously used in pesticides and personal care products) and polycyclic musks (personal care products) were amongst the other persistent organic pollutants investigated. The programme is unique in the range of waste materials and organic contaminants under investigation and will provide vital information necessary to inform the development of a methodology and quality standards to assess the suitability of new waste materials for recycling in agriculture.

This paper presents the findings of the initial stages of the research programme. The specific objectives addressed in the paper are: i) identify and describe at least two representative examples of each recycled waste types used in agriculture as fertilisers and soil amendments or as bedding for livestock production; ii) assess the chemical properties of the waste materials including a range of priority organic contaminant compounds that may present a potential risk to the human food chain; and iii) examine the chemical properties of the wastes in comparison to the scientific literature, available standards for waste materials and the concentrations of the compounds in environmental samples.

Materials and Methods

Selection, collection and sampling of waste materials

The materials under investigation were biosolids (treated sewage sludge), MBMA, PLA, representative of a range of recycled waste materials currently applied to agricultural land in the UK as sources of plant nutrients, and PSA, used as an agricultural liming agent. Additionally, compost like output (CLO) from the mechanical biological treatment (MBT) of municipal solid waste (MSW) was included as it has future potential as a source of nutrients in agriculture. A range of recycled materials used as livestock bedding have been selected, including recycled waste wood (RWW), dried paper sludge (DPS) from paper manufacturing and PSA, which is used as a desiccant in livestock bedding. A high degree of variability in the chemical composition of the materials was expected; hence, at least two examples within each waste category were collected where possible to increase the probability of finding a material containing the compounds of interest. Details of the wastes selected for the programme are provided in Table 1. The materials listed were collected or delivered by the company and stored in a cool agricultural storage shed.

Representative composite sub-samples of each waste were collected for analysis. The biosolids and CLO were sub-sampled at collection at the production site, and the remaining materials were sampled shortly after delivery. Sub-samples of approximately

3 kg fresh weight (FW) of each of the waste materials were collected and delivered to the Food and Environment Research Agency (Fera, York) in cool boxes with ice-packs by overnight courier. The sub-samples (except for the wood wastes) were collected in 1 L food-grade polypropylene containers lined with dichloromethane (DCM) swabbed aluminium foil. The wood wastes were collected in 5 L polypropylene containers, also lined with DCM swabbed foil. Additional sub-samples of biosolids and CLO were provided for DEHP analysis; approximately 1 kg of each material was collected in glass duran bottles, which had been prepared by heating in a muffle furnace at 400ºC for 4 hours. Dichloromethane - swabbed foil was placed between the bottle and the lid.

On receipt at Fera, biowastes (biosolids and CLO) were frozen prior to analysis, whereas dry wastes (RWWs, ash, DPS) were stored as received. Samples were mixed thoroughly before sub-sampling prior to preparation and extraction for organic contaminant analysis.

An additional set of sub-samples of approximately 500g of each waste was collected in 1 L polypropylene containers and delivered to a NAMAS accredited laboratory (NRM Laboratories, Bracknell) for routine physico-chemical analysis.

Organic contaminant analysis

Polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs), polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs)

The method used for the preparation, extraction and analysis of samples (Fernandes *et al.*, 2004; 2008) forms part of the CEN method – EN16215:2012 for PCDD/F and PCB analysis (CEN, 2012). In brief, samples were fortified with ^{13}C-labelled analogues of target compounds and exhaustively extracted using mixed organic solvents. PBDEs and ortho substituted PCBs/PBBs were separated from non-ortho substituted PCBs/PBBs, PCDD/Fs and PBDD/Fs by fractionation on activated carbon. The two fractions were further purified using adsorption chromatography on alumina. Analytical measurement was carried out using high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) for all analytes apart from the *ortho*-substituted PCBs which were analysed by high resolution gas chromatography-unit resolution mass spectrometry (HRGC-LRMS).

The analysis is accredited (UKAS) to ISO 17025 standards, with the inclusion of an in-house reference material and method blanks which were evaluated prior to reporting of sample data and used to determine the limits of detection. Further quality assurance measures included the successful participation in available international inter-comparison exercises such as Dioxins in Food-2011 to 2014, EURL run PT exercises,

etc. on dioxins, dioxin-like PCBs, ICES-6 PCBs and PBDEs. Additionally, quality control evaluation for the accompanying data follows the criteria specified for chlorinated dioxins and PCBs (EC, 2012).

Mixed halogenated dibenzo-p-dioxins/dibenzofurans (PXDD/Fs) and mixed halogenated biphenyls (PXBs)

The methodology used for the determination of PXDD/Fs and PXBs has been described in detail by Fernandes *et al*. (2011). In brief, a representative sample aliquot was fortified with nine ^{13}Carbon labeled internal standards (a mix of eight, Br-Cl substituted dioxins, furans and biphenyls, and 2,3,7,8-TCDD), and allowed to equilibrate for at least one hour. The sample was blended and purified on a multilayer acid/base-modified silica column. This was followed by dual activated carbon column fractionation of the mono-ortho substituted PXBs from the di-tetra ortho substituted PXBs (discarded), and the non-ortho substituted PXBs and the PXDD/Fs. The extracts resulting from both fractions were analysed by HRGC-HRMS (high resolution gas chromatography- high resolution mass spectrometry) at a resolution of 13,500 to 15,000 res. The measurements were performed on a Micromass Autospec Ultima high resolution mass spectrometer coupled to a Hewlett Packard 6890N gas chromatograph fitted with a 60 m x 0.25 mm i.d. J&W DB-5 MS fused silica capillary column (0.25μm

film thickness) and a programmable temperature vaporisation (PTV) injector operated in constant flow (~1 ml/min helium) mode.

Polycyclic aromatic hydrocarbons (PAHs)

The following analytes were determined (regulated contaminants (EU, 2011) are highlighted in bold):

acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, benzo[c]fluorene, pyrene, benzo[e]pyrene, benzo[b]naptho[2,1-d]thiophene, anthanthrene, coronene, benzo[ghi]fluoranthene, **benz[a]anthracene**, **chrysene**, **benzo[b]fluoranthene**, benzo[j]fluoranthene, benzo[k)fluoranthene, **benzo[a]pyrene**, cyclopenta[c,d]pyrene, indeno[123cd]pyrene, dibenzo[ah]anthracene, benzo[ghi]perylene, dibenzo[al]pyrene, dibenzo[ae]pyrene, dibenzo[ai]pyrene, dibenzo[ah]pyrene and the substituted PAH, 5-methylchrysene

The PAH analytical methodology (Rose *et al*., 2007) is based on internal standardisation (13-Carbon) with GC-MS measurement. An aliquot of the homogenised sample was fortified with ^{13}C-labelled analogues of target compounds and saponified with methanolic potassium hydroxide. The extracted PAH solutions were purified in two stages with a DMF/cyclohexane partition followed by adsorption chromatography on activated silica. A sensitivity standard was added to the purified extracts and these were measured using HRGC LRMS.

Hexabromocyclododecanes (HBCDs), pentabromocyclododecene (PBCD) and tetrabromobisphenol A (TBBPA)

The analyses were carried out in duplicate. Sample aliquots including a procedural blank and a reference material were fortified with [13]Carbon labelled analogues of TBBPA, αHBCD, βHBCD, and γHBCD, allowed to stabilise, blended with hexane:dichloromethane, 60:40 (v/v) and the matrix hydrolysed using acid modified silica. The extract recovered from this process was filtered, washed, concentrated and solvent exchanged to a methanol:water solvent system prior to analysis by HPLC-MS/MS in the multiple reaction monitoring mode (MRM) mode.

The parameters used for evaluating data quality, were similar to those used for other analyses. Method limits of detection, evaluated through method blank determinations were typically $<0.01 \mu g \ kg^{-1}$ whole weight and analytical recoveries were generally within the range of 50 - 100%. There are no certified reference materials available for HBCD or TBBPA analysis in relevant matrices. However, aliquots of all the samples analysed were fortified with native analytes and the concentrations of recovered analytes measured, were in good agreement with fortification levels. Additionally a fortified in-house reference material was also analysed regularly with the samples and returned values that were in good agreement with fortification levels.

Polychlorinated napthalenes (PCNs)

A full description of the reagents, reference standards and procedures used for the extraction and analysis has been reported by Fernandes *et al.* (2010). In brief, samples were fortified with ^{13}C-labelled analogues of target compounds and exhaustively extracted using mixed organic solvents. PCNs were chromatographically fractionated from potential interferents such as PCBs, using activated carbon. The extract was further purified using adsorption chromatography on alumina. Analytical measurement was carried out using high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS). Additional control was provided by the inclusion of methods blanks and a reference material.

The quality control criteria used for evaluating data are very similar to the accredited methodology used for the chlorinated dioxins and PCBs (Fernandes *et al*., 2010). There are no available reference materials (RMs) specific to PCNs, but the same material that is used for PCDD/F and PCB analysis (cod liver oil), was analysed during the course of this work with results showing good consistency and agreement with established values.

Screen for perfluorochemicals (PFCs)

The sample extraction procedure applied is described by Lloyd *et al*. (2009). Briefly, quadruple 1-10 g portions of each homogenised sample were weighed out into Falcon tubes (50 ml). The appropriate volumes of internal standard (IS) and standard

addition mixtures were added, to prepare two unspiked portions, one overspiked at the reporting level (1 µg kg^{-1}) and one portion at 10-times the reporting level (10 µg kg^{-1}). The sample portions were homogenised for 1-3 mins as required in 20 ml of methanol with an Ultra Turrax (T25 basic with S25N blade). When homogenised, more methanol was added (ca. 40 ml in total) and mixed, while withdrawing the Ultra Turrax blade. Samples were agitated overnight (16h), then centrifuged (15 min, 5000 rpm). The supernatant methanol extracts were evaporated under a nitrogen stream (80°C, in silyanised glass vials) just to dryness, and the residues were re-dissolved in aqueous KOH (25 ml, 0.01 M, sonication 10 min). The aqueous extracts were then re-centrifuged (15 min, 5000 rpm). When required, the supernatants were poured in one continuous gentle movement, without breaking up the floating materials, or disturbing the sediment, into a funnel connected onto the top of a preconditioned SPE cartridge (weak anion exchange). The cartridges were loaded at a constant drip rate, by increasing from gravity feed to full vacuum as required. After loading, the cartridges were washed with ammonium acetate (2 x 6 ml, 25 mM, pH 4.5) and eluted with basic methanol (4 ml, 0.1% ammonia). The eluates were reduced under a stream of nitrogen gas (60°C), just to dryness and the residues taken up in methanol (400 µl, sonication 10 min). Extracts were transferred into silyanised glass microvials (300 µl) for LC-MS/MS determination.

Analysis was undertaken by LC-MS/MS. A CTC Pal autosampler (Presearch, UK) and an HP1100 HPLC system with column oven (Agilent, UK) were coupled to an API4000 triple quadrupole mass spectrometer (MDS Sciex Instruments, UK). The guard cartridge was C8. The HPLC column (5 µm, 60A, 2.1 x 150 mm) was Fluorosep RP Octyl phase, thermostatically held at 30ºC in the column oven. The injection volume was generally 10 µl. The gradient programme (methanol: aqueous ammonium formate, 5 mM, pH 4) was: 10% methanol increasing to 30% at 0.1 min (linear gradient), to 75% at 7 min and 100% methanol at 10 min, this was held for 5 min (column washing), then decreased to 10% methanol at 15.1 min, this was held 4.9 min at 10% methanol (column re-conditioning). The eluate was diverted to the mass spectrometer between 7 and 19.5 min, and from 0-7 and 19.5-20 min it was discarded by valve switching to waste, in order to protect the ion source. Analyst 1.4.2 software was used for instrument control, file acquisition and peak integration. The MS detector in multiple MRM mode with a Turbo Ion Spray source was used for quantitative analysis. Data acquisition was conducted in one simultaneous acquisition schedule without separation into chromatographic acquisition windows. Instrumental parameters were optimised by infusion of standard solutions directly into the MS detector (1 µg ml^{-1} in 1:1 methanol: aqueous ammonium formate (5 mM, pH 4). The Turbo Ion Spray (TIS) conditions were; turbo-gas 50 psi, curtain-gas 12 psi, nebuliser-gas 50 psi, desolvation temperature

450°C. An Excel spreadsheet was used to calculate PFC concentrations from the standard additions.

Gas chromatography-time of flight-mass spectrometry (GC-TOF-MS) screen

Duplicate portions of each sample (between 3 and 10 g depending upon the physical form of the sample) were transferred to a glass vial. Acetonitrile (20 mL) was added, and the vials were capped and shaken for 18 hours on an orbital shaker. The vials were centrifuged (2000 rpm for 10 minutes) and the solvent transferred to a clean glass vial before evaporation at 40°C. The residue was re-dissolved in acetonitrile (1 mL), vortex mixed and transferred to a vial for GC-TOF-MS analysis. Standards for a number of target compounds were also prepared including phthalates, chloroparaffins, chlorinated benzenes, polycyclic musks (PCMs) and 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE).

The standards and extracts were analysed by gas chromatography with time-of-flight mass spectrometric detection using a 7890B GC system and a 7200 Accurate-mass QTOF GC/MS (Agilent, Santa Clara, CA, USA) along with a Gerstel Multiflex Sampler (Anatune, Cambridge, UK). Chromatographic separation was achieved on ZB-Semi volatiles column, 30 m long x 0.25 mm i.d. x 0.25 µm film thickness (Phenomenex, Cheshire, UK). Injection (1 µL) of each extract was carried out using the multi-mode inlet set at 280°C with total flow 54 mL minute^{-1} and helium (1 mL minute^{-1}

constant flow) was employed as the carrier gas. The oven temperature was held at 80°C for 3 minutes before being ramped at 10°C minute^{-1} until 320°C and then held for 5 minutes. The transfer line was held at 280°C and TOF-MS detection was carried out with the ion source in electron impact mode with source temperature at 230°C and a fixed emission current of 35 µA. The mass range measured was m/z 50–500 with an acquisition rate of 5.0 spectra second^{-1}. Mass calibration was carried out after every second injection at m/z 68.9947 and 365.9895.

Results and Discussion

General physico-chemical properties of waste materials

The biosolids were collected from two of the largest treatment plants in the UK serving highly populated areas and accepting combined sewage flows from domestic and industrial inputs, and were selected as they represented potentially worst-case examples of contemporary biosolids chemical contamination. The biosolids had dry solids (DS) contents of 19.5-19.8%, and pH values of 8.4-8.6 (Table 2), which are as expected for mechanically dewatered biosolids (e.g. Rigby *et al.* 2009; Rigby and Smith, 2013). The volatile solids (VS) content of one biosolids sample (Biosolids2) was 62%, which is typical for biosolids from mesophilic anaerobic digestion. However, the sample collected from a different source wastewater treatment plant, Biosolids1, had a

higher VS content of 73.6%, indicating that the biosolids were less well stabilised during treatment compared to Biosolids2. The N contents of the biosolids were 4.7 and 6.0% for Biosolids2 and Biosolids1, respectively, which are typical for this treatment type. The biosolids products were also a source of other plant nutrient elements: P, K, Mg, S, Ca, Fe, Mo, Mn and B.

The concentrations of potentially toxic elements (PTEs) in Biosolids1 were less than or similar to the median concentrations for biosolids used in agriculture (Table 3), with the exception of Zn, which was 739 mg kg^{-1} DS, greater than the median concentration of 574 mg kg^{-1} DS. However, the concentrations of PTEs in Biosolids2 were generally significantly greater than the median concentrations shown in Table 3, with the exception of Pb, which had a slightly lower concentration. The concentrations of PTEs in both sources of biosolids were within acceptable limits for application to the soils under investigation in this research programme according to the Sludge Use in Agriculture Regulations (SI, 1989). However, the concentration profiles of PTEs detected in Biosolids1 indicated this material generally had a greater contamination status compared to the biosolids sample from Biosolids2. Nevertheless, the relatively moderate PTE contents found in both sources of biosolids samples (Table 2) demonstrated the overall improvement in biosolids chemical quality, reflecting reduced industrial and domestic inputs, compared to historical contaminant concentration data (eg Smith, 1997; 2009a).

The CLOs had similar DS contents of 76.6% for CLO1 and 76.8% for CLO2, and VS contents of 55.8% and 56.2% for CLO1 and CLO2, respectively. These values were significantly lower than the VS contents measured for the biosolids products and were consistent with the higher degree of stabilisation achieved by composting processes, although, this may also reflect lower inputs of volatile organic matter in the organic fraction of MSW (OFMSW). The total N contents were 1.5% DS and 2.6% DS for CLO1 and CLO2, respectively. These values were lower than for the biosolids reflecting the lower N content of the OFMSW feedstock compared to sewage sludge; additionally, losses of N via ammonia volatilisation would be expected during the composting process. The CLOs were also a source of other plant nutrients, in particular they were a significant source of K, containing 0.67% DS and 1.1% DS of total K for CLO1 and CLO2, respectively, compared to a total K content in the biosolids equivalent to 0.1-0.2% DS. The concentrations of PTEs were similar to or less than the concentrations in the biosolids, with the exception of Pb, which, at 191 mg kg^{-1} and 201 mg kg^{-1} DS for CLO1 and CLO2, respectively, was greater than the concentrations of total Pb measured in the biosolids, which were 92.6-107 mg kg^{-1} DS. The concentrations of PTEs in the CLOs were within suitable limits for agricultural application, relative to acceptable biosolids quality values (Table 3 and also see Smith, 2009b).

The ash materials appeared physically as dry, finely divided minerals and, as would be expected, the DS contents were large and between 88.8% for PLA2 to 99.9% for PSA. The VS contents were also small, due to the destruction of organic matter during combustion. The PSA had a VS content <0.01%; however, the VS contents of the MBMAs and PLAs were equivalent to 2.4-6.8% DS, indicating the presence of a small residual amount of organic matter in these ash types. The pH of the ash materials was alkaline and similar in the range of pH 12.3-12.7. The PSA in particular had a high neutralising value of 46.8% w/w, which is close to the typical value reported for agricultural lime of 50-55% w/w (Defra, 2010). The ash materials were not significant sources of N, as this is lost to the atmosphere during combustion; however, the MBMAs and PLAs were significant sources of P and K. The MBMAs contained 9.7 - 12.4% DS of total P, and 2.8 2.9% DS total K. Conversely, the PLA samples had greater K contents than P contents equivalent to 5.1% and 7.7% DS total P and 11.2% and 12.1% total K for PLA1 and PLA2, respectively.

In general the concentrations of PTEs in the ashes were smaller than those in the biosolids and CLOs. However, PLA2 had a greater concentration of As at 12.1 mg kg^{-1} DS, compared to values between 3.0-8.5 mg kg^{-1} DS for the biosolids, CLOs and other ash materials. The Zn content of the PLA samples was 1394-1673 mg kg^{-1} DS; this was larger than the other ash types examined and was similar to biosolids, which contained 739-1930 mg kg^{-1} DS of total Zn. The Pb content of PLA2 was 186 mg kg^{-1} DS; this

was also increased compared to other ash samples and was in a similar range to the CLO products, which contained 191-201 mg kg^{-1} DS of total Pb. Theoretical calculations of the rates of application of PTEs to soil, if the ash materials were applied at maximum agronomic rates indicated that none of the ash materials exceeded the maximum loading rates according to the Sludge Use in Agriculture Regulations (SI, 1989). The PTE concentrations in all the ash materials fell below the maximum compositional values for trace elements allowed in the PLA Quality Protocol (WRAP and EA, 2012) for the use of PLA as an agricultural fertiliser.

Three of the RWWs were classified as Grade A (RWW1, RWW3 and RWW4), and one was classified as Grade C (RWW2) according to the PAS111 Specification for the Requirement and Test Methods for Processing Waste Wood (Wrap, 2012). Only the Grade A wastes are classified as suitable for use as animal bedding. Three of the RWW samples tested were composed of fine wood chips, including the RWW2, RWW3 and RWW4 products. The Grade A RWW1 was wood shavings. The materials contained moderate to small amounts of moisture and had DS contents in the range of 74.6% for RWW4 to 89.8% for RWW1. As would be expected for a cellulose/lignin based material, the RWWs contained relatively low concentrations of plant nutrient elements. In general, the concentrations of PTEs were also relatively low compared to the other materials examined. However, RWW1 had an As concentration of 9.8 mg kg^{-1} DS, which was slightly greater than the concentration of 8.5 mg kg^{-1} DS measured in

Biosolids2. A high concentration of Pb was also found in this material, equivalent to 238 mg kg^{-1} DS, which exceeded the concentrations of this element present in the CLOs of 191-201 mg kg^{-1} DS.

The kiln-dried paper sludge (DPS) had a high DS content of 97.2%, a VS content of 33.7% and a neutral pH value of 7.2. As might be expected for material derived from wood, it was not a significant source of plant nutrient elements with concentrations of N, P, K, Mg and S in the same range, or similar to the RWWs. The concentrations of PTEs were low and similar to those observed for the PSA.

Polychlorinated dibenzo-p-dioxin (PCDD), polychlorinated dibenzofuran (PCDF) and polychlorinated biphenyl (PCB) concentrations

The greatest ∑ WHO$_{2005}$-TEQ value for PCDD/Fs was measured for MBMA1, at 83.1 ng kg^{-1} DS (Table 4), more than 32 times the median ambient concentration in rural UK soils (2.42 ng WHO$_{1998}$-TEQ kg^{-1} dry soil (ds), Table 5), and 14 times greater than the concentration in urban UK soils (5.92 ng WHO$_{1998}$-TEQ kg^{-1} ds, Table 5). The remainder of the WHO$_{2005}$-TEQ values were less than 20 ng kg^{-1} DS, with the exception of RWW1, which had a WHO$_{2005}$-TEQ value of 26.3 ng kg^{-1} DS. Toxic impurities of PCDD/Fs are typically found in wood that has been treated with the preservative pentachlorophenol (PCP) (Davou, 2014), and so the presence of PCDD/Fs in RWW1 was not unexpected. The RWW is required to undergo a visual inspection process

(WRAP, 2012) to remove contaminated wood, however, it is unsurprising that this process cannot entirely eliminate sources of contamination. It was interesting to note that RWW1, a Grade A recycled wood, had greater PCDD/F concentrations than RWW2, a Grade C material.

The lowest WHO_{2005}-TEQ values were detected for PSA, PLA1, and RWW4 with upper bound values of 0.12 ng kg^{-1} DS, 0.91 ng kg^{-1} DS, and 1.33 ng kg^{-1} DS respectively, lower than the median concentrations found in UK soils (Table 5). The WHO_{2005}-TEQ values for the two biosolids were similar, although Biosolids2 had a slightly greater value of 12.4 ng kg^{-1} DS compared to 10.5 ng kg^{-1} DS for Biosolids1. The total concentrations of PCDD/Fs in the biosolids materials was 433-558 ng kg^{-1} DS, which were significantly lower than the historical mean concentration for sewage sludge reported by Smith (2009a) of 2178 ng kg^{-1} DS. The upper bound WHO_{2005}-TEQ of 10.5-12.4 ng kg^{-1} DS was approximately four times that of the median ambient dioxin concentration in rural UK soils of 2.42 ng WHO_{1998}-TEQ kg^{-1} ds, and only approximately twice the median dioxin concentration of 5.92 ng WHO_{1998}-TEQ kg^{-1} ds for urban soils. Of the two CLOs, CLO1 had the greatest WHO_{2005}-TEQ of 18.2 ng kg^{-1} DS compared to 11.2 ng kg^{-1} DS for CLO2.

The PCDD/F concentrations in the materials were generally significantly lower than European limits and proposed limit values for these compounds in biosolids, composts and PLA (Table 6). For example, the concentrations in biosolids were

approximately 10 times smaller than the proposed EC (2003) limit for PCDD/Fs in biosolids of 100 ng TEQ kg^{-1} DS. However, the concentration in MBMA1 exceeded the maximum limit in the PLA Quality Protocol (Wrap and EA, 2012) of 20 ng WHO_{2005}-TEQ kg^{-1} DS by approximately 4 times. It is feasible that the greater PCDD/F concentration measured in this ash material may have potentially arisen due to the co-combustion of detergent washings and sludges, associated with food preparation and processing activities, with meat and bone meal at this facility (Table 1) (Sonnenburg and Nichols, 1995; Zarczynski *et al*., 2002), assuming the detergents were chlorine-containing. Differences in the mode of operation of incineration processes between biomass combustion plants are also likely to be a major source of variation in the chemical composition of residual ash products (Gong, 2014). However, it should be noted that the analytical results presented here may only provide a snapshot of the compositional properties of the waste products examined, and do not test the statistical variability and characteristics of the materials.

The dominant dioxin congener was OCDD, present in indicative concentrations between 1172-1987 ng kg^{-1} DS in the biosolids samples and RWW3, 3247-3296 ng kg^{-1} DS in the CLOs, and 16479 ng kg^{-1} DS and 11071 ng kg^{-1} DS for RWW1 and RWW2, respectively. Additionally, 1,2,3,4,6,7,8-HpCDD was found in concentrations of 1185 ng kg^{-1} DS for RWW1, and was also present in high concentrations 269.5 – 985.6 ng kg^{-1} DS in several other materials (Biosolids2, MBMA1, Biosolids1, CLO2, RWW2 and

CLO2). Furans found in relatively high concentrations were the related congeners: OCDF and 1,2,3,4,6,7,8-HpCDF. The greatest concentrations of OCDF were found in RWW1 and RWW2, at 811.8 and 500.0 ng kg^{-1} DS, respectively.

The largest $\sum$WHO$_{2005}$-TEQ values obtained for (dioxin-like) non-Ortho PCBs (PCBs 77, 81, 126 and 169) were measured in the biosolids and were 1.07 ng kg^{-1} DS and 1.66 ng kg^{-1} DS for Biosolids1 and Biosolids2, respectively, and for MBMA1 the TEQ was 1.68 ng kg^{-1} DS (Table 7). The congener present in the greatest concentrations was PCB77, at 255.2-263.7 ng kg^{-1} DS in CLO, and 192-239 ng kg^{-1} DS in biosolids (Table 7). Additionally, PCB77 was present at relatively high concentrations in RWW in the range 81-108 ng kg^{-1} DS.

For the Ortho-PCBs (Table 8), the greatest values for the $\sum$ICES 6 congeners (which are all non-dioxin like PCBs) were measured in the biosolids samples and were 41.0 µg kg^{-1} DS for Biosolids2 and 17.3 µg kg^{-1} DS for Biosolids1. The CLOs also had relatively high values of $\sum$ICES 6, equivalent to 15.7-17.1 µg kg^{-1} DS, and similar values were present in samples of RWW, 11.2-17.1 µg kg^{-1} DS. The $\sum$ WHO$_{2005}$-TEQ values for the dioxin-like ortho PCBs (PCBs 105, 114, 118, 123, 156, 167 and 189) were relatively low and in the range 0.004 ng kg^{-1} (MBMA1, MBMA2, PLA1 and PLA2) to 0.29 ng kg^{-1} DS (Biosolids 2). For those waste types that contained greater concentrations of PCBs (biosolids, CLOs and RWW1 and 2), a number of congeners were generally present in concentrations greater than 1 ng kg^{-1} DS, but less than 10 ng

kg^{-1} DS; these 10 congeners included: PCB18, PCB28, PCB31, PCB47, PCB49, PCB52, PCB101, PCB118, PCB138, PCB153 and PCB180. The other eight congeners, PCB51, PCB105, PCB123, PCB128, PCB156, PCB157, PCB167 and PCB189, tended to be present in concentrations < 1 ng kg^{-1} DS.

The total PCB concentrations in the biosolids (29.6-73.2 µg kg^{-1} DS) and CLOs (25.7-29.9 µg kg^{-1} DS) were significantly greater than the median concentration of PCBs in rural and urban UK soils of 1.01 µg kg^{-1} ds and 1.84 µg kg^{-1} ds, respectively (Table 5). However, concentrations were significantly lower than mean sum of PCBs in sewage sludge reported from earlier surveys of sludge quality by Smith (2009a) of 220 µg kg^{-1} DS, and the mean sum of PCBs in CLO reported by Amlinger (2004) of 730-1680 µg kg^{-1} DS. Additionally, the PCB concentrations in biosolids and CLOs were significantly lower than the concentrations in various standards and proposed standards across Europe (Table 6). The total concentration in MBMA2, 3.23 µg kg^{-1} DS, and the RWWs, 6.0-27.0 µg kg^{-1} DS, exceeded the concentration typically found in UK rural and urban soils. However, the total sums of PCBs in the remaining ashes (the PLAs, MBMA1 and PSA) were lower than the median concentrations in UK soils.

The findings indicated that the concentrations of PCDD/Fs and PCBs in representative, contemporary waste materials used in agriculture were generally relatively low, below proposed limit values and for several of the waste materials the concentrations were within the range in UK soils, and that they were generally

considerably smaller than previously reported results from historical surveys of biosolids and CLO materials. The results demonstrated the beneficial impact of the controls on PCDD/Fs and PCBs introduced in the 1980s-90s in reducing significantly the primary sources of PCDD/Fs and PCBs in the environment (Smith and Riddell-Black, 2007), which is reflected in the relatively low concentrations of these principal persistent organic pollutants (POPs) observed in contemporary waste samples.

Polybrominated dibenzo-p-dioxin (PBDD), dibenzofuran (PBDF) and polybrominated biphenyl (PBB) concentrations

The total concentrations of PBDD/Fs in the biosolids samples were 2303 and 4414 ng kg^{-1} DS for Biosolids1 and Biosolids2, respectively (Table 9). Venkatesan and Halden (2014) analysed 12 PBDD/Fs in composited archived biosolids that were collected in 32 US States and the District of Columbia from 94 wastewater treatment plants as part of the US EPA national sewage sludge survey in 2001. Two PBDDs and five PBDFs were detected in the biosolids (all of which were detected in the present study), with a total mean concentration of 10,000 ng kg^{-1} DS (range 630-42,800); this was approximately 2-4 times greater than the total concentrations found in the biosolids samples measured here. However, the WHO$_{2005}$-TEQ values were 40.3 ng kg^{-1} DS for Biosolids1 and 78.0 ng kg^{-1} DS for Biosolids 2 (Table 9), and were similar to the mean WHO$_{2005}$-TEQ contribution observed by Venkatesan and Haldan (2014) of 72 ng kg^{-1}.

The WHO$_{2005}$-TEQ contribution from PBDD/Fs measured here was 4-7 times greater than the WHO$_{2005}$-TEQ for PCDD/Fs (10.5-12.4 ng kg^{-1} DS) and was consistent with Venkatesan and Haldan (2014), who also found a significantly greater WHO$_{2005}$-TEQ contribution from PBDD/Fs than their chlorinated analogs.

The CLOs had lower WHO$_{2005}$-TEQ values than the biosolids of 18.0-32.2 ng kg^{-1} DS (Table 9). PBDD/Fs and PBBs may be present as impurities in commercial brominated flame retardants (Venkatesan and Haldan, 2014), which explains their presence in municipal biosolids and CLO derived from MSW.

The concentrations of PBDD/Fs in the other materials were significantly lower than for the biosolids and CLOs, with upper bound WHO$_{2005}$-TEQ generally <1 ng kg^{-1} DS, with the exception of PLA2 and RWW1, which had WHO$_{2005}$-TEQ of 5.11 and 3.05 ng kg^{-1} DS respectively (Table 9). PBDD/Fs may be formed during the combustion of products that contain polybrominated diphenylether (PBDE) (Venkatesan and Halden, 2014). However, the small concentrations of PBDD/Fs detected in most of the ash materials collected for this investigation were expected because they generally consisted of feedstocks that were unlikely to contain PBDEs. For example, PSA is produced from the combustion of paper manufacturing sludge only and PLA2 is produced from the ash from a straw-burning plant and poultry litter biomass power plant (Table 1).

The congener present in the greatest concentration was 1,2,3,4,6,7,8-HeptabromoBDF, with values in the range 716-4151 ng kg^{-1} DS. This congener represented 94% of the total mass of BDD/BDF congeners found in biosolids samples and this observation was consistent with the results reported by Venkatesan and Halden (2014). Additionally, 1,2,3,4,7,8-HexaBDF was also present in concentrations between 53.2 for CLO1 to 132 ng kg^{-1} DS for Biosolids2.

The greatest WHO$_{2005}$-TEQ values for non-ortho PBBs were recorded for the CLOs with upper bound values of 0.039-0.042 ng kg^{-1} (Table 10). The WHO$_{2005}$-TEQ values for the biosolids were lower at 0.022-0.019 ng kg^{-1} DS. The other materials had WHO$_{2005}$-TEQ values of 0.003-0.011 ng kg^{-1} DS. These concentrations were lower than those measured for the chlorinated analogs (Table 7).

Overall, the contributions of PBDD/Fs and dioxin like PBBs to the WHO$_{2005}$-TEQ values for biosolids, were equivalent to 40.3-77.9 ng kg^{-1} DS compared to 11.5-14.0 ng kg^{-1} DS for PCDD/Fs and PCBs. Thus, risk assessments that only consider PCDD/Fs and PCBs may underestimate the potential total toxicity of dioxin-like compounds present in environmental media.

The ortho-PBBs were present in low concentrations in the waste samples, and generally below the detection limit (Table 11). However, certain congeners, for example, BB-15 and BB-153 were detected in the biosolids and RWW at concentrations between 0.0024 - 0.037 µg kg^{-1} DS. The concentrations of ortho-PBBs were

significantly smaller than those of ortho-PCBs (Table 8). In comparison to their chlorinated counterparts, there has been little research to date on the presence of PBDDs, PBDFs and PBBs in biosolids, other wastes and in the environment. Hence, this data forms some of the first to be reported on PBDD/Fs concentrations in waste samples from the UK.

Mixed halogenated dibenzo-p-dioxin (PXDD), dibenzofuran (PXDF) and mixed halogenated biphenyl (PXB) concentrations

The concentrations of PXDD/Fs and PXBs in waste samples are presented in Tables 12 and 13. For several of the waste materials, including PLA1, PSA, RWW3 and RWW4 most or all of the individual congeners were below detection limits. However, for the biosolids, CLOs, MBMAs, PLA2 and RWW 1 and 2, between 7-11 of the congeners were detected. The congeners found in the greatest concentrations were 2-Br-3,6,7,8,9-ClDx, which was present at 1.07 ng kg^{-1} DS in PLA2, and 2-Br-7,8-ClDf present at concentrations of up to 1.36 ng kg^{-1} DS in Biosolids2. The total sum of PXDD/Fs that could be quantified is significantly lower than for PCDD/Fs or PBDD/Fs (Tables 4 and 9). However, the compounds measured here are a small sub-set of the potentially large number of laterally substituted (and hence, potentially toxic) mixed halogenated congeners. Theoretically, there are 337 possible PXDDs and 647 possible PXDFs with bromo- or chloro- substituents in the 2,3,7,8 positions, including 13 tetra-

substituted and 90 penta-substituted congeners (Fernandes *et al.*, 2014). Thus, there are

numerous possible combinations of mixed halogenated dioxins and biphenyls that

correspond to each laterally substituted PCDD/F or PCB congener, and only one or two

of each combination were analysed. For example, the polychlorinated 1,2,3,7,8,-PeCDF

exists as a single congener, but there are 30 possible mixed halogenated analogues and

only two of these have been analysed (1Br2,3,7,8,ClDF and 1,3Br2,7,8ClDF).

Practically, the limited range of primary and [13]Carbon labeled analytical standards that

are currently available for PXDD/F analysis also hinders the reliable measurement of a

larger selection of mixed halogenated compounds. The WHO_{2005}-TEQ values for mixed

halogenated dioxins and biphenyls could not been calculated because the dataset of

congeners was not comprehensive, and additionally there is insufficient information

available to define robust toxic equivalence factors (TEFs) for the PXDDs and PXDFs.

Nevertheless, the contribution of these diverse groups of compounds to the overall

WHO_{2005}-TEQ could be significant considering the many possible mixed halogenated

congeners.

Polycyclic aromatic hydrocarbon (PAH) concentrations

The results for from an initial assessment of 4 significant PAH congeners (EFSA,

2008) in the waste samples are presented in Table 14. The values indicated that the

greatest concentrations of PAHs were present in the biosolids, CLOs and RWWs (with

the exception of RWW3). Of the two biosolids samples, Biosolids2 had the greater

$\sum$PAH4 value, equivalent to 719 µg kg^{-1} DS compared to 414 µg kg^{-1} DS for

Biosolids1. The CLO2 sample had a larger $\sum$PAH4 content compared to CLO1 of 563

µg kg^{-1} DS compared to 336 µg kg^{-1} DS, respectively (Table 12). The Grade C RWW2,

had the largest $\sum$PAH4 value of 390 µg kg^{-1} DS, compared to RWW1 and RWW3,

which contained 342 and 285 µg kg^{-1} DS, respectively. The concentrations of PAHs in

the two biosolids samples were lower than those reported by Jones *et al*. (2014) for

primary and secondary sludge from UK wastewater treatment plants. For example

Biosolids1 and Biosolids2, the concentrations of benzo(a)pyrene and

benzo(b)fluoranthene were 19 and 87 µg kg^{-1} DS and 23 and 22 µg kg^{-1} DS,

respectively, whereas Jones *et al*. (2014) reported median concentrations of 320 µg kg^{-1}

and 310 µg kg^{-1}. The biosolids in the present study had undergone anaerobic digestion

whereas the primary and secondary sludges investigated by Jones *et al*. (2014) had not

received further treatment. However, it is unlikely that the lower concentrations

observed for Biosolids1 and 2 were due to removal during anaerobic digestion, as PAHs

are highly resistant to biodegradation, and previously removals of only approximately

10% have been observed for benzo(a)pyrene and benzo(b)fluoranthene under normal

mesophilic digestion conditions (Trably *et al.*, 2003). The concentrations of $\sum$PAH4 in

biosolids, CLO, and RWW1 and 2 were similar to or greater than the median value

measured for rural soil in the UK of 296.4 µg kg^{-1} ds (Table 5). However, the

concentrations measured in waste samples were smaller than the median content in UK urban soil of 1433 µg kg^{-1} ds.

The concentrations of PAH measured in the biosolids and CLO samples were significantly lower than the limits existing or proposed for PAHs in biosolids and composts, however, it is important to note the values in the standards are for greater numbers of PAH congeners (Table 6). The PAH concentrations in the ash samples were significantly smaller compared to the other waste types examined. For ash product, the largest ∑PAH4 concentration was found in PLA2 at 97 µg kg^{-1} DS compared to values in the range of 0-17 µg kg^{-1} DS for the other ash types. The low concentrations of PAHs in the waste materials are consistent with the declining burden of these compounds in the UK environment (Smith and Riddell-Black, 2007).

Polybrominated diphenyl ether (PBDE) and deca-brominated diphenyl ether (BDE)/brominated biphenyl (BB)

The concentrations of PBDEs in the waste samples are presented in Table 15. Biosolids contained more PBDEs compared to the other waste materials tested equivalent to 90.1-103.2 µg kg^{-1} ∑PBDEs DS. Knoth *et al.* (2007) reported the median PBDE concentration for sewage sludge from 11 wastewater treatment plants, based on the sum of 6 significant congeners (28, 47, 99, 153, 154 and 183), was 108 µg kg^{-1} DS. For the same 6 congeners, the concentration in the biosolids samples measured here was

slightly lower and in the range 77-88 µg kg^{-1} DS. Jones *et al*. (2014) reported median

concentrations of 21, 33, 6, 5 and 5 µg kg^{-1} for BDEs 47, 99, 100, 153 and 154 in sludge

from UK wastewater treatment plants; these median values were very similar to the

corresponding PBDE concentrations we detected in Biosolids1 and Biosolids2. The

CLOs also contained relatively high concentrations of PBDEs with total concentrations

equivalent to 40.5-59.5 and 40.5 µg kg^{-1} DS. The ∑PBDEs in the other waste samples

was relatively low and in the range 0.52-4.34 µg kg^{-1} DS. PBDEs are destroyed during

waste combustion treatment processes, therefore the small concentrations detected in

the ash samples were as expected (North, 2004).

The PBDE congeners present in the greatest concentrations were BDE-28/33 and

BDE-99. The concentrations of BDE-28/33 in biosolids and CLO were in the ranges

32.9-25.3 µg kg^{-1} and 10.4-12.9 µg kg^{-1} DS, respectively. The concentration of BDE-99

in the biosolids samples was 25.0-42.0 µg kg^{-1} DS and was 11.9 - 15.1 µg kg^{-1} DS in

CLO. The BDE-99 congener is one of the main constituents of commercial penta-BDE

formulations, which may explain its relatively high abundance (Smith and Riddell-

Black, 2007). In addition BDE-49, BDE-66, BDE-100, BDE-153, BDE-154 and BDE-

183 were generally present in the biosolids and CLOs at concentrations between 1-10

µg kg^{-1} DS, whereas the remaining PBDEs congeners were present in concentrations <1

µg kg^{-1} DS.

The biosolids samples contained the largest amounts of deca-BDE, followed by CLO and RWW (Table 16). Biosolids2 contained an indicative concentration of 6693 µg kg^{-1} DS compared to 4198 µg kg^{-1} DS in Biosolids1. The deca-BDE 209 content in the biosolids samples were greater than the concentrations measured by Knoth *et al*. (2007) in sewage sludge samples from 11 municipal wastewater treatment plants in Germany, which contained a median value of 108 µg kg^{-1} (range 12.5-288 µg kg^{-1}). Both CLO samples had similar concentrations of deca-BDE in the range 1650-1723 µg kg^{-1} DS and the RWW1 and RWW2 samples also contained appreciable amounts of deca-BDE in the range 143.0-246.1 µg kg^{-1} DS, reflecting the use of deca-BDEs as flame-retardants including in furniture manufacturing. The relatively high concentrations of deca-BDE-209 in comparison to the penta- and octa- BDEs (Table 15), reflected the expanding use of deca-BDEs in Europe, since the prohibition of preparations containing penta and octa-BDE by the European Union in 2003 (EU, 2003). However, in 2012, Deca-BDE was listed by the European Chemicals Agency (ECHA) as a substance of very high concern, and has since been proposed for listing under the Stockholm Convention for Persistent Organic Pollutants (POPs) (EC, 2004); its status as a POP is currently under review.

The concentrations in the other RWWs, the PLAs, and the MBMAs were small and between 0.704 µg kg^{-1} DS for MBMA2 to 11.0 µg kg^{-1} DS for RWW4. The deca-BB-209 concentrations were significantly lower compared to deca-BDE and ranged

between 0.009 - 11.0 µg kg^{-1} DS for RWW2 and 3, to 0.479 11.0 µg kg^{-1} DS for CLO1. Again, low concentrations of deca-BDEs were anticipated for the ash materials as they are destroyed during waste incineration (North, 2004).

Hexabromocyclododecanes (HBCDs), pentabromocyclododecene (PBCD) and tetrabromobisphenol A (TBBPA) concentrations

Results of the analysis for the brominated flame-retardants: HBCD, PBCD, TBBPA, are presented in Table 17. The largest concentrations of HBCDs were found in the CLOs, biosolids and RWW1 and were broadly in similar ranges in these materials. For example, biosolids samples contained the largest amounts of γ-HBCD in the range 302-390 µg kg^{-1} DS.

TBBPA was the next most significant compound detected of this group of brominated flame-retardants and the biosolids samples contained similar amounts of TBBPA in the range 33-45 µg kg^{-1} DS. α-HBCD was present in the greatest concentrations in CLO2, between 139-836 µg kg^{-1} DS, and TBBPA was present in the greatest concentrations in CLO1, between 493-517 µg kg^{-1} DS. α-HBCD was also present in the largest amounts in CLO at 121-302 µg kg^{-1} DS for CLO2 and 26-70 µg kg^{-1} DS for CLO1, and CLO2 also contained the most β-HBCD, equivalent to 34-78 µg kg^{-1} DS, compared to the other waste sample types examined. PBCD was also elevated in CLO compared to the other waste materials tested; overall, the largest concentration of PBCD was measured

in CLO2, between 42-351µg kg^{-1} DS, and CLO1 contained a smaller amount between 13-29 µg kg^{-1} DS. The largest concentrations of this group of brominated flame-retardants measured in RWW were generally detected in RWW1, which contained67-169 µg kg^{-1} DS of γ-HBCD and 19-45 µg kg^{-1} DS of α-HBCD. The results also indicated that these compounds were detected at elevated amounts in RWW2, but the concentrations were generally smaller compared to RWW1, for instance the γ-HBCD content in RWW2 was equivalent to 21.2 µg kg^{-1} DS. However, RWW2 potentially contained the largest overall amount of TBBPA detected in the RWW samples examined with an indicative concentration of 52 µg kg^{-1} DS for and TBBPA. HBCDs, PBCD and TBBPA were also detected in the RWW3 and 4, although concentrations were generally very small and typically ≤1 µg kg^{-1} DS. The relatively large concentrations of these flame-retardants in CLO originating from the organic fraction of MSW, biosolids and, in some cases, in RWW may be expected because they are found in many materials in the domestic environment including fabrics, packaging materials and plastics (Smith and Riddell-Black, 2007).

Concentrations of these brominated flame-retardants were generally below detection limits in the ash materials. However, TBBPA was detected in PLA1 at 42 µg kg^{-1} DS, and α- and β- HBCD were also detected, although at very low concentrations ≤0.12 µg kg^{-1} DS or less. These two stereoisomers, plus γ-HBCD were also detected at very low concentrations in MBMA2, at ≤0.13 µg kg^{-1} DS. The results from the analysis

of waste ash materials were therefore consistent with the near complete destruction of HBCDs observed by MSW incineration (Mark *et al.*, 2015).

Polychlorinated napthalene (PCN) concentrations

The PCN data are presented in Table 18 and showed the largest amounts of this compound group were found in the biosolids, CLO and RWW1 samples. CLO1 had the largest overall $\sum$PCN concentration of 1977 ng kg^{-1} DS, compared to 680 ng kg^{-1} DS for CLO2. Biosolids1 contained a similar $\sum$PCN compared to CLO2, equivalent to 742.5 ng kg^{-1} DS, and Biosolids2 contained 541 ng kg^{-1} DS of $\sum$PCN. The $\sum$PCN values detected here are therefore significantly smaller than mean PCN concentrations in sewage sludge reported by Smith (2009a) and Clarke and Smith (2011) of 83,000 ng kg^{-1} DS (range 5000-190,000 ng kg^{-1} DS) and 44,000 ng kg^{-1} DS, respectively, and suggest that PCNs have further diminished as biosolids contaminants since these reviews of earlier surveys of sewage sludge chemical quality were reported.

Waste wood potentially contained more $\sum$PCN than the biosolids and CLO samples. Thus, RWW1 contained 1210 ng kg^{-1} DS of $\sum$PCN, followed by RWW2 with of 603.5 ng kg^{-1} DS . Samples RWW3 and 4 contained generally similar amounts of $\sum$PCN, in the range 88.3-120.5 ng kg^{-1} DS (as upper bound values). The range of maximum (upper bound) $\sum$PCN values measured in the ash materials examined was

between 8.8 ng kg^{-1} DS in PLA1 to 107.9 ng kg^{-1} DS in MBMA2, respectively. The concentrations of PCNs in PSA were all below the limit of detection.

The PCNs in greatest concentrations were PCN 52 and 53 present between 103.7-379.3 ng kg^{-1} DS and 194.6-737.3 ng kg^{-1} DS, respectively, in the biosolids, CLOs, and RWW1 and 2 samples. CLO1 and RWW1 also contained PCN 69 in relatively larger concentrations compared to the other materials tested of 223.1 and 130.0 ng kg^{-1} DS, respectively, and PCN71/72 at 369.7 and 203.0 ng kg^{-1} DS, respectively. The remaining PCNs were generally present in the materials at concentrations less than 100 ng kg^{-1} DS.

PCNs have not been produced in the UK for over 35 years. Current potential sources are expected to be dominated by the disposal routes of capacitors and engine oil, where the majority of manufactured PCNs were used (Smith and Riddell-Black, 2007). PCNs have also been found in fly ash and flue gas from waste incineration and landfills are also expected to be a source of PCN emissions (Smith and Riddell-Black, 2007). However the introduction of improved standards of waste incineration may increase the destruction of PCNs during combustion (Noma *et al.*, 2006). The low concentrations measured in the waste samples collected for this programme therefore reflect the declining emission and concentrations of PCNs in the environment.

Screen for perfluoroalkyl chemicals (PFCs)

An initial screen was conducted for the presence and abundance of PFCs in the waste materials (results not presented). Perfluorochemicals were present in the greatest concentrations in the biosolids samples. Preliminary results indicated that concentrations of perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDeA) and perfluorooctane sulfonate (PFOS) were present in concentrations greater than 10 µg kg^{-1} DS in Biosolids1. The results indicated that PFDeA and PFOS were also present in concentrations greater than 10 µg kg^{-1} DS in Biosolids2, and, in addition, perfluoroundecanoic acid (PFUnA) was present in concentrations greater than 10 µg kg^{-1} DS in this biosolids sample. The screen for PFCs in biosolids indicated that the concentrations of the majority of remaining PFCs investigated were between 1-10 µg kg^{-1} DS. Preliminary findings indicated that the concentration of PFCs were generally smaller than the ranges and mean values of PFOS and PFOA in biosolids reported by Clarke and Smith (2011); the mean concentrations for these compounds estimated in that study were equivalent to196 µg kg^{-1} DS and 75 µg kg^{-1} DS, respectively. Perfluorochemicals were also detected in concentrations greater than 1 µg kg^{-1} DS, but generally less than 10 µg kg^{-1} DS in the CLOs and the RWWs, in particular RWW1. In addition, PFOA was found at concentrations greater than 10 µg kg^{-1} DS in CLO1, and RWW1. Further work will be conducted to quantify the PFC concentrations in the biosolids, CLO and RWW samples.

Gas chromatography-time of flight-mass spectrometry (GC-ToF-MS) screen

The presence and concentrations of several other groups of priority compounds was identified using a GC-ToF-MS screen approach as described in the Materials and methods Section.

The wastes were examined for a number of phthalate substances, nine of the samples contained one or more of dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), dibutyl phthalate (DBP), di(2-ethylhexyl)phthalate (DEHP), diisononyl phthalate (DiNP) and diisodecyl phthalate (DiDP), up to estimated concentrations of 32 mg kg^{-1} DS (in CLO2). The greatest concentrations were observed in the CLOs, followed by the biosolids samples. Concentrations of DEHP in biosolids (15 mg kg^{-1} DS) were in the range reported by Clarke and Smith (2011) for biosolids of <0.02-3515 mg kg^{-1} DS, although lower than the mean value of 58 mg kg^{-1} DS. The DEHP concentrations measured in the biosolids samples were similar to the mean and median concentrations of 19 and 11 mg kg^{-1} for DEHP in sludge from UK wastewater treatment plants reported by Jones *et al*. (2014).

The waste samples were examined for short chain chloroparaffins (CPs) (C10-C1) and medium chain CPs (C14-C17). Medium chain CPs were detected in Biosolids2 and CLO1 at approximate concentrations of 9 and 3 mg kg^{-1} DS, respectively, but short chain CPs were not detected. The concentration in biosolids was significantly lower than the mean concentration of medium chain CPs of 910 mg kg^{-1} DS reported by Clarke and Smith (2011).

The chlorobenzenes (CBs), hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) were detected at very low values, approximately 0.5 µg kg^{-1} DS in the biosolids, and HCB only was found in the CLOs.

The polycyclic musk (PCM), tonalide was detected in the biosolids at concentrations of approximately 850-900 µg kg^{-1} DS and in the CLOs at concentrations of 39-52 µg kg^{-1} DS. Galaxolide was detected in the CLOs at concentrations of 299-455 µg kg^{-1} DS, and was also detected in the biosolids, although quantification was not possible. Clarke and Smith (2011) reported mean concentrations of galaxolide and tonalide in biosolids of 141 and 365 µg kg^{-1} DS, respectively.

Further work is required to quantify the phthalates, CPs, CBs and PCMs in the wastes in which they were detected and to examine their transfer to food products in the crop and dairy investigations.

The GC-ToF-MS screen also indicated the presence of several other organic contaminants of potential interest in the waste samples. The brominated flame-retardant 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) was detected in small amounts in both CLO samples. The wood preservative pentachlorophenol (PCP) was detected in two of the recycled waste wood samples (RWW1 and 2), and a degradation product of PCP, pentachloroanisole, was detected in CLO2 and RWW2. Additionally the organophosphate flame-retardant, tris(2-chloroisopropyl)phosphate (TCCP) was detected in 8 of the samples (Biosolids1, CLO1, CLO2, PLA2, MBMA1, RWW1,

RWW2, RWW4) and tris(2-chloroethyl)phosphate (TCEP) was observed in PLA2 and Biosoids1. These compounds and their metabolites are of interest due to their toxicity and potential persistence and accumulation in the food chain and will be investigated further in the waste materials and the transfer investigations to crops and milk.

Conclusions

In general, the consignments of waste materials obtained for this investigation contained relatively low concentrations of organic contaminants. Notably, the concentrations of PAHs, PCDDs/Fs and PCBs present in biosolids, CLOs and ash were significantly lower than proposed and implemented limit values for these compounds across Europe for biosolids, composts and recycled ash materials where available. For example, the TEQ of PCDD/Fs was approximately 10 times less than the proposed EC (2003) limit for biosolids applied to agricultural land of 100 ng TEQ kg^{-1} DS. The concentrations of PAHs in biosolids samples was also approximately 10 times less than the proposed limit of 6 mg kg^{-1} DS (EC, 2003), and the concentrations of PCBs were approximately 10-50 times smaller than the proposed limit of 0.8 mg^{-1} kg DS (EC, 2003). Additionally, the TEQ of PCDD/Fs present in PLA samples fell below the maximum limit of 20 ng TEQ kg^{-1} in the UK Quality Protocol for the production and use of PLA. However, PBDD/Fs were also detected in the biosolids and CLOs, and these contributed significantly to the overall TEQ. The individual congeners of mixed

halogenated PXDD/Fs that could be analysed were present only in low concentrations. However, only a small proportion of all the potential PXDD/Fs congeners could be quantified, hence the potential contribution of PXDD/Fs to the overall TEQ is uncertain. PBDE brominated flame retardants were detected in the biosolids, CLOs and RWWs in small concentrations, but, as may be expected, were not found in the ash materials. The materials were also screened for a wide range of compounds using a GC-ToF-MS approach. Further work is required to quantify phthalates, CPs, CBs, PCMs, organophosphate flame-retardants, BTBPE and PCP in the wastes in which they were detected and to examine their transfer to food products in the crop and dairy investigations.

The concentrations of principal groups of POP compounds measured in the waste samples are smaller compared to previous reports. This suggests that controls implemented to reduce environmental emissions have been effective in achieving significant reductions in the primary sources of POP release to the environment (Smith and Riddell-Black, 2007).

The research programme will provide detailed information on the potential transfer to the foodchain of organic contaminants in waste materials recycled in agriculture. This new and quantitative data will aim to improve the robustness of risk assessments and confidence in the use of these materials in agriculture, and establish guidelines where necessary to protect the food chain.

Acknowledgements

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Table 1 Description of wastes used in agriculture or with potential to be used in agriculture collected for the research programme

Type	Sample ID	Waste Description
Biosolids	Biosolids1	Pre-pasteurised, dewatered, mesophilic anaerobically digested wastewater treatment sludge, 6 weeks on cake storage pad. Collected from a large treatment works, serving a population of 2.1 M accepting combined domestic and industrial wastewater.
	Biosolids2	Dewatered, mesophilic anaerobically digested wastewater treatment sludge. Conventional treatment status AD - 36-38ºC, Hydraulic Retention Time (HRT) 15-18d, followed by 9 days HRT secondary digestion in liquid pathkill tanks; 14 days on cake pad. Collected from large treatment works, serving a population of 1.75 M accepting combined domestic and industrial wastewater.
Compost like output (CLO) from MBT	CLO1	The mechanically separated organic fraction of MSW is composted, under forced aeration with daily turning, in two phases, for 6 weeks. The final refining stage removes all materials over 12mm and heavyweight particles. CLO is currently used for land restoration. It is tested weekly for *E. coli* and *Salmonella* and is animal by-product compliant. Selected due to high level of refinement compared to other materials currently produced.
	CLO2	The mechanically separated <50mm organic fraction (approximately 42% of original MSW) undergoes in-vessel composting. Oversized material from greenwaste composting is blended with maturation material (passed through two barriers and the maturation pad) in a ratio of 2:1. The fresh shredded organic fraction is blended with the 2:1 blend at a ratio of 4:1 to improve aeration. The material spends <14 days in Barrier 1, followed by Barrier 2, where it is required to reach a temperature of 60ºC, followed by 4 weeks on a maturation pad. Selected due to high level of refinement compared to other materials currently produced.

Table 1 cont.

Type	Sample ID	Waste Description
Meat and bone meal ash (MBMA)	MBMA1	The MBMA is produced in a fluidised bed incineration plant. The feedstock is a minimum of 80% animal tissue waste, plus a maximum of 20% sludges from cleaning during the preparation and processing of foods of animal origin, dairy industry wastes, non-hazardous pharmaceutical waste, edible oils and fats, compost liquor from QP and PAS 100 compliant plants, and detergent washings. Combustion temperatures are >850 ^{o}C in bed, and ~ 900-950 ^{o}C in freeboard (air above bed). The amount of ash produced is 10,000 -11,000 t pa (from ~ 50,000 t of MBM). Ash is ~80% fly ash, 20 % bed ash. The MBMA has End-of-Waste approval.
	MBMA2	Feedstock for fluidised bed MBM combustion plant is from Defra compliant renderers. MBMA produced has End-of-Waste approval.
Poultry litter ash (PLA)	PLA1	PLA is Quality Protocol compliant.
	PLA2	The final product is a blend of fly ash and bottom ash from a straw-burning plant and poultry litter biomass power plants sites. PLA is Quality Protocol compliant.
Paper sludge ash (PSA)	PSA	PSA is produced by combustion of paper manufacturing sludge in a fluidised (or 'bubbling') bed combustor that uses sand at its base. The bed is kept at around 500°C while the super-heaters in the chamber increase the temperature to circa 750°C at the summit. The ash is filtered in the baghouse and distributed to 4 storage silos. Only paper sludge is added to the combustor; no other physical material is used. There is a small amount of natural gas used to supplementary fire the kiln when needed. The fly ash is the bulk of the ash produced. There are technically two grades of fly-ash depending on particle size; the chemical composition is equivalent. The baghouse ash is predominantly a coarser material compared to filtered ash. Both types of ash are blended together in the silos. The ash is classified as hazardous due to its high pH and is not currently used in agriculture, although an End of Waste application was pending for land application at the time of collection.
Recycled wood waste (RWW)	RWW1	Dairy cattle bedding: wood shavings from recycled Grade A wood.
	RWW2	Dairy cattle bedding: wood chip from Grace C wood.
	RWW3	Dairy cattle bedding: wood chip from recycled Grade A wood. Particle size < 10mm.
	RWW4	Wood chip from recycled Grade A wood.
Dried paper sludge (DPS)	DPS	Kiln dried paper sludge from recycled paper processing.

Table 2 General physico-chemical characteristics of wastes collected for the research programme (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	DPS	RWW			
	1	2	1	2	1	2	1	2			1	2	3	4
DS (%)	19.5	19.8	76.6	76.8	96.1	88.7	89.7	88.8	99.9	97.2	89.8	84.6	87.2	74.6
VS (%)	73.6	62	55.8	56.2	2.40	6.66	6.84	5.21	<0.01	33.7	96.3	99.4	99.7	98.8
pH	8.4	8.6	8.3	8.0	12.7	12.5	12.3	12.4	12.5	7.2	6.1	5.4	5.8	5.9
Lime equivalent as $CaCO_3$ (% w/w)	6.2	9.7	9.6	8.4	39.8	23.1	40.7	27.7	85.5	52.1	<2	<2	<2	<2
Neutralising value as CaO (%w/w)	3.5	5.4	5.4	4.7	22.2	12.6	22.8	15.5	46.8	29.2	<1	<1	<1	<1
Conductivity (μS cm^{-1})	1670	1700	4440	7660	2150	2610	35700	4200	9810	1135	896	936	384	231
Total N (%w/w)	5.99	4.68	1.49	2.60	<0.01	0.33	<0.01	0.06	0.30	0.40	1.05	1.02	0.51	0.31
Nitrate N (mg kg^{-1})	<10	<10	<10	63.8	<10	34.9	15.6	27	<10	<10	26.7	37.8	<10	<10
Ammonium N (mg kg^{-1})	7104	6461	562	2414	<10	34.9	<10	<10	<10	29.8	128	528	20.7	26.8
Total P (mg kg^{-1})	21311	29980	4441	4783	97634	124882	51243	77794	752	202	1734	185	287	962
Total K (mg kg^{-1})	1333	2230	6741	11009	28236	28927	112520	121135	1115	183	2151	730	1131	799
Total Mg (mg kg^{-1})	3654	5937	5208	5816	6602	8405	32858	23927	11960	2144	1026	317	440	524
Total S (mg kg^{-1})	13746	14249	4781	12111	16522	15144	26673	33649	2072	668	1059	414	17.1	619
Total Ca (mg kg^{-1})	41379	48142	53272	49466	274179	278814	184002	174255	484036	188621	10423	2815	2364	2834
Total Fe (mg kg^{-1})	8241	42533	10400	12065	5074	3210	4629	6476	3175	883	1565	409	284	2232
Total Mo (mg kg^{-1})	8.59	20.8	10.4	4.55	2.71	3.81	11.2	24.8	1.99	<1	1.18	<1	<1	<1
Total Mn (mg kg^{-1})	357	783	370	337	130	234	1774	1802	201	85.5	146	86.6	78.6	112

Table 2 cont.

	Biosolids		CLO		MBMA		PLA		PSA	DPS	RWW			
	1	2	1	2	1	2	1	2			1	2	3	4
Total B (mg kg^{-1})	25.7	62.8	22	22.5	48	19.8	141	88.5	20.5	4.4	11.5	9.2	7.1	7.9
Water Soluble Mg (mg kg^{-1})	48.8	69.1	168	675	0.99	6.32	1.98	2.48	0.21	155	120	60.3	33.6	46.7
Water Soluble P (mg kg^{-1})	546	516	68.8	52	0.71	45.7	23.2	1279	2.06	4.1	34.5	21.5	22.9	16
Water Soluble K (mg kg^{-1})	509	1192	4103	7907	12699	24803	83296	89527	64.4	45.7	624	442	495	580
Water Soluble S (mg kg^{-1})	519	426	2902	9337	10157	14735	20862	25942	18.1	397	567	205	65.8	132
Water Soluble Ca (mg kg^{-1})	247	433	997	4123	8666	121	64.4	19.6	9850	1212	728	321	70.9	125
Total As (mg kg^{-1})	4.06	8.49	6.78	6.54	3.48	<3	3.99	12.2	3.86	<3	9.82	12.1	<3	<3
Total Cd (mg kg^{-1})	1.15	2.34	2.53	1.68	0.59	0.44	0.72	1.56	0.26	0.189	0.31	0.46	0.16	0.21
Total Cu (mg kg^{-1})	430	446	267	287	105	92.9	310	324	317	45.6	37.7	42.4	17.1	14.2
Total Zn (mg kg^{-1})	739	1930	551	615	340	430	1394	1673	64.1	2.15	144	50.2	25.3	52
Total Hg (mg kg^{-1})	1.12	0.81	0.32	0.24	<0.02	0.02	<0.02	0.12	0.05	0.041	0.05	<0.02	<0.02	<0.05
Total Ni (mg kg^{-1})	30.5	127	44.9	39.1	6.34	6.99	12.1	16.8	16	6.35	2.73	<1	<1	3.36
Total Pb (mg kg^{-1})	92.6	107	191	201	36.1	35.7	14.5	186	12.9	18.38	238	53	5.95	15.9
Total Cr (mg kg^{-1})	42.7	213	67.6	32.4	18.1	18.8	11.0	31	31.5	28.6	17.8	18.5	2.09	4
Fluoride [100:1 H$_2$SO$_4$] (mg kg^{-1})	151	456	47.4	81.1	370	118	145	131	286	32.2	<10	<10	<10	<10
Se (mg kg^{-1})	4.69	3.82	0.2	0.42	1.92	1.66	3.68	4.77	0.19	<0.09	<0.09	<0.09	<0.09	<0.09

CLO: compost-like-output; MBMA: meat and bone meal ash; PLA: poultry litter ash; PSA: paper sludge ash, DPS: dried paper sludge; RWW: recycled wood waste

Table 3 Median concentrations of PTEs in biosolids used in agriculture (Gendebien *et al.*, 2008)

PTE	Median concentration mg kg^{-1} DS
Cd	1.3
Cr	61
Cu	295
Hg	1.2
Ni	30
Pb	112
Zn	574

Table 4 Polychlorinated dibenzodioxins/dibenzofurans (PCDD/DF) concentrations in the waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**		**1**	**2**	**3**	**4**
						ng kg^{-1} DS							
2,3,7,8-TCDD	0.28	0.68	0.25	0.26	10.22	0.39	0.09	1.23	<0.02	0.29	0.35	0.03	0.04
1,2,3,7,8-PeCDD	1.4	2.56	1.02	1.05	35.40	1.66	<0.35[a]	4.55	<0.03	1.27	0.71	0.33i	0.11
1,2,3,4,7,8-HxCDD	1.12	2.26	1.96	1.39	27.45	2.14	0.21	4.28	<0.05	2.80	1.87	0.18	0.16
1,2,3,6,7,8-HxCDD	13.17	12.42	19.41	8.16	53.80	5.02	0.56	10.14	0.03	26.02	13.87	1.75	1.34
1,2,3,7,8,9-HxCDD	4.36	5.25	6.66	3.87	36.82	3.51	0.30	6.81	<0.03	7.12	3.22	0.62	0.48
1,2,3,4,6,7,8-HpCDD	441	269	985.6	459.6	269.5	43.20	3.00	72.82	<0.6	1185[b]	607.57	68.90	44.97
OCDD	1987[b]	1172[b]	3247[b]	3296[b]	256.0	76.20	6.88	182.4	<2.82	16479[b]	11071[b]	1174[b]	643.5
2,3,7,8-TCDF	4.01	5.48	2.92	3.32	37.42	1.91	0.58	5.99	<0.06	1.14	0.87	0.28	0.26
1,2,3,7,8-PeCDF	1.29	3.76	2.28	2.36	26.97	2.81	0.41[a]	4.12	<0.07	0.81	0.60	0.14	0.15
2,3,4,7,8-PeCDF	1.86	4.48	3.63	3.16	35.30	4.46	0.40[a]	5.78	<0.07	1.47	0.80	0.21	0.26
1,2,3,4,7,8-HxCDF	2.19	5.75	3.38	3.74	18.51	4.36	0.33	2.78	<0.07	4.47	2.54	0.41	0.36
1,2,3,6,7,8-HxCDF	1.9	4.89	2.96	2.89	23.33	5.43	0.36	3.51	<0.04	3.36	1.63	0.31	0.26
1,2,3,7,8,9-HxCDF	0.23	0.61	0.17	0.31	1.99	0.60	0.04	0.21	<0.01	0.27	0.15	0.11	0.03
2,3,4,6,7,8-HxCDF	2.44	5.28	4.48	4.21	28.41	9.58	0.62	4.03	<0.05	5.59	2.49	0.50	0.35
1,2,3,4,6,7,8-HpCDF	26.97	35.36	27.62	46.30	40.78	18.68	1.07	7.49	0.13	209.4	121.8	14.00	12.42
1,2,3,4,7,8,9-HpCDF	1.61	4.08	2.00	2.43	7.17	5.56	0.20	0.99	<0.05	10.29	6.31	0.77	0.58
OCDF	54.15	71.3	58.55	79.38	10.96	12.77	2.81	5.17	<0.76	811.8	500.0	42.86	27.91
Sum TEQ[c] lower	10.52	12.35	18.16	11.21	83.05	7.43	0.57	12.27	<0.01	26.34	14.82	2.05	1.33
Sum TEQ[c] upper	10.52	12.35	18.16	11.21	83.05	7.43	0.91	12.27	0.12	26.34	14.82	2.05	1.33
Sum[d]	2545	1605	4370	3918	920.0	198.3	18.22	322.3	4.89	18750	12336	1305	733.2

[a], indicative due to analyte suppression on instrument; b, indicative out of linear range; [c]WHO$_{2005}$-TEQ; d, concentration of congeners <limit of detection (LOD) assumed to = LOD
CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood

Table 5 Median concentrations of organic contaminants in UK soils (μg kg^{-1} dry soil (ds)), except where indicated

Compound	Area	Median/50 percentile	95 percentile
PCDD/F	Rural (UK)	2.42 ng WHO$_{1998}$-TEQ kg^{-1} [a]	18.0 ng WHO$_{1998}$-TEQ kg^{-1} [a]
	Urban (UK)	5.92 ng WHO$_{1998}$-TEQ kg^{-1} [b]	
PCBs (Sum of total)	Rural (UK)	1.01[a]	5.51[a]
	Urban (UK)	1.86[c]	
PAHs	Rural (UK)[a]	2240 [a]	7503 [a]
PAHs (Sum 4)	Rural (UK)	296.4[d]	
	Urban (UK)	1433[d]	

[a]UKSHS (2007a); [b] UKSHS (2007b); [c]UKSHS (2007c); [d]UKSHS (2007d)

Table 6 Standards and proposed standards for maximum concentrations of selected organic contaminants in sewage sludge (Smith, 2009a), compost (Saveyn and Eder, 2014) and ash (WRAP and EA, 2012), compared to concentrations found in this study

		PCDD/Fs (ng TEQ kg^{-1} DS)[a]	PCBs (mg kg^{-1} DS)	PAHs (mg kg^{-1} DS)
Biosolids	EC (2003)	100	0.8[b]	6[c]
	Denmark			3[c]
	Sweden		0.4[b]	3[d]
	Lower Austria	100	0.2[e]	
	Germany	100[f]	0.2[e]	
	France		0.8[b]	
	Biosolids1	*11*	*0.017[g]*	*0.41[h]*
	Biosolids2	*12*	*0.041[g]*	*0.72[h]*
Compost	Saveyn and Eder (2014)	30	0.2 (PCB$_7$)	6 (PAH$_{16}$)
	Austria	20[f]	0.2 (PCB$_6$)	6
	Belgium		0.8 (PCB$_6$)	
	Germany	[i]	[i]	
	France		0.8 (PCB$_6$)	
	Luxembourg	20[fj]	0.1[j]	10 (PAH$_{16}$)[j]
	Slovenia		0.4 (1st class); 1 (2nd class PCB$_6$)	3
	Switzerland	20[fj]		4 (PAH$_{16}$)[j]
	CLO1	*18*	*0.017[g]*	*0.18[h]*
	CLO2	*11*	*0.015[g]*	*0.11[h]*
PLA	UK Quality Protocol	20[k];10[l]		
	MBMA1	*83*	*0.0003[g]*	*0.001[h]*
	MBMA2	*7.4*	*0.002[g]*	*0.023[h]*
	PLA1	*0.91*	*0.0004[g]*	*0.017[h]*
	PLA2	*12*	*0.0004[g]*	*0.097[h]*
	PSA	*0.12*	*0.0004[g]*	*0.0003[h]*

PCDD/Fs, polychlorinated dibenzo-p-dioxins and dibenzo-p-furans; PCBs, polychlorinated biphenyls; PAHs, polycyclic aromatic hydrocarbons

CLO = compost-like-output; MBMA = meat and bone meal ash; PLA = poultry litter ash; PSA = paper sludge ash

[a]Unless specified TEQ system (I-TEQ, WHO$_{1998}$-TEQ, WHO$_{2005}$-TEQ) not reported; [b]sum of seven congeners (PCB 28, 52, 101, 118, 138, 153, 180); [c]sum of nine congeners (acenapthene, fluorene, phenanthrene, fluoranthene, pyrene, benzo[*b+j+k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, indeno[1,2,3-*c,d*]pyrene); [d]sum of six congeners; [e]each of six congeners (PCB 28, 52, 101, 138, 153, 180); [f]I-TEQ; [g]sum of ICES 6 (PCB 28, 52, 101, 138, 153, 180); [h]PAH$_4$ (benz(a)anthracene, chrysene, benzo[b]fluoranthene , benzo[a]pyrene); [i]maximum sum of PCDD/F and dl-PCB = 30 ng WHO-TEQ kg^{-1} D, in some cases additional restrictions for PCDD/F of 5 ng WHO-TEQ kg^{-1} DM; [j]guide value; [k]maximum (ng WHO$_{2005}$-TEQ kg^{-1}); [l]average for each 10 samples or each shipment (ng WHO$_{2005}$-TEQ kg^{-1})

Table 7 Non-ortho polychlorinated biphenyl (PCB) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	2	1	2	1	2	1	2		1	2	3	4
	ng kg^{-1} DS												
PCB 77	192i	239i	263.71	255.2	25.70	4.23	4.23	9.73	3.11	108.43	81.29	17.34	42.81
PCB 81	7.81i	9.01i	12.79	11.59	5.36	<0.52	<0.47	1.28	<0.42	5.89	4.13	0.83i	2.19
PCB 126	9.87	15.62i	6.50	7.10	15.36	0.69	0.33	3.24	<0.15	3.60	1.77	0.86	1.19
PCB 169	1.95	2.39	1.10	1.20	4.51	0.35	0.57 [a]	1.09	<0.51	0.33	0.20	0.15	<0.35
TEQ[b] lower	1.07	1.66	0.72	0.77	1.68	0.08	0.03	0.36	<0.01	0.38	0.19	0.09	0.12
TEQ[b] upper	1.07	1.66	0.72	0.77	1.68	0.08	0.06	0.36	0.03	0.38	0.19	0.09	0.13
Total	211.6	266.0	84.10	275.1	50.93	5.78	5.60	15.35	4.19	118.25	87.39	19.18	46.54

[a] = indicative due to analyte suppression on instrument; [b]WHO$_{2005}$-TEQ;
CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood

Table 8 Ortho-polychlorinated biphenyl (PCB) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**		**1**	**2**	**3**	**4**
						µg kg^{-1} DS								
PCB18	1.85	6.22	3.69	1.76	<0.05	0.19	<0.08	<0.07	<0.07	2.31	4.00	<0.05	0.52
PCB28	2.64	6.07	3.94	2.15	<0.08	1.34[a]	0.12	0.20	<0.11	2.52	3.22	0.75	0.66
PCB31	2.15	7.55	4.06	2.28	0.08	0.53[a]	<0.12	0.09	<0.11	2.61	3.22	0.60	0.70
PCB47	1.36	1.61	0.80	0.64	0.03	0.24[a]	<0.08	0.02	<0.07	0.35	0.31	0.11	0.12
PCB49	1.47	2.87	1.62	1.18	<0.04	0.17[a]	<0.07	<0.06	<0.06	0.92	0.84	0.19	0.13
PCB51	0.23	0.32	0.13	0.08	<0.01	<0.01	<0.02	<0.01	<0.02	0.09	0.09	0.02	0.03
PCB52	3.24	8.46	3.24	2.27	<0.05	0.32	<0.09	<0.07	<0.08	1.63	1.26	0.41	0.77
PCB99	1.04	2.55	0.73	0.63	<0.02	0.03[a]	<0.04	0.02	<0.04	0.53	0.24[a]	0.15	0.20
PCB101	2.63	7.39	2.31	2.15	0.04	0.07	<0.07	<0.06	<0.06	1.92	0.96	0.54	0.59
PCB105	0.78	2.34	0.77	0.74	0.02	0.02	0.03	0.02	0.02	0.61	0.24	0.15	0.20
PCB114	0.09	0.10	0.05	0.04	<0.01	<0.01	0.01	<0.01	<0.01	0.03	0.01	<0.01	0.01
PCB118	2.07	5.84	1.72	1.55	0.04	0.05	0.07	0.05	<0.06	1.40	0.57	0.37	0.47
PCB123	0.05	0.08	0.04	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.04	<0.01	0.01
PCB128	0.45	1.08	0.40	0.36	<0.01	<0.01	<0.01	<0.01	<0.01	0.40	0.14	0.09	0.11
PCB138	3.58	8.06	3.05	3.23	0.05	0.05	0.07	0.06	<0.05	3.76	1.73	0.93	0.82
PCB153	3.24	7.08	2.60	3.16	0.03	0.03	0.06	0.03	<0.05	3.53	1.91	0.81	0.64
PCB156	0.35	0.82	0.26	0.26	0.01	<0.01	<0.01	<0.01	<0.01	0.32	0.13	0.08	0.08
PCB157	0.09	0.19	0.05	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	0.04	0.02	0.01
PCB167	0.12	0.30	0.09	0.10	<0.01	<0.01	<0.01	<0.01	<0.01	0.10	0.05	0.03	0.03
PCB180	1.92	3.93	2.00[a]	2.70	0.01	<0.01	<0.01	0.01	<0.01	3.70	2.16	0.60	0.35
PCB189	0.03	0.09	0.03	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.02	<0.01	<0.01
						Sum of ICES 6								
lower	17.25	40.99	17.14	15.7	0.14	1.80	0.19	0.30	<0.01	17.05	11.24	4.04	3.83
upper	17.25	40.99	17.14	15.7	0.27	1.82	0.41	0.43	0.36	17.05	11.24	4.04	3.83
						Sum of ICES 7								
lower	46.83	18.86	17.21	0.17	1.79	0.32	0.35	0.00	18.46	11.81	4.41	4.3	19.32
upper	46.83	18.86	17.21	0.3	1.87	0.49	0.48	0.42	18.46	11.81	4.41	4.3	19.32
TEQ[b] (ng kg^{-1})	0.107	0.293	0.090	0.085	0.004	0.004	0.005	0.004	0.004	0.078	0.033	0.020	0.025
Sum (total)	29.38	72.95	29.60	25.43	0.63	3.22	1.00	0.85	0.88	26.88	20.92	5.94	6.47

CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood
[a], indicative; [b], Sum TEQ for dioxin-like ortho PCBs (105, 114, 118, 123, 156, 167 and 189)

Table 9 Polybrominated dibenzodioxin (PBDD) and dibenzofuran (PBDF) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	2	1	2	1	2	1	2		1	2	3	4
							ng kg^{-1} DS						
237-TriBDD	0.176	0.230	0.296	0.26	0.069	<0.059	0.010	0.104	<0.005	0.039	0.072	0.053	0.020
2378-TetraBDD	0.096	0.190	0.282	0.186	0.067	<0.036	0.008	<0.035	<0.006	<0.019	0.028	<0.019	<0.046
12378-PentaBDD	2.25	2.67	1.406	0.87	<0.035	<0.038	<0.027	<0.044	<0.024	<0.021	<0.026	<0.019	<0.370
123478/123678-HexaBDD	23.43	25.4	14.7	1.43	<0.087	<0.086	<0.061	2.216	<0.06	<0.042	<0.047	<0.044	ab
123789-HexaBDD	14.9	15.7	8.49	0.96	<0.112	<0.121	<0.044	0.950	<0.044	<0.059	<0.067	<0.061	ab
238-TriBDF	10.2	25.8	7.83	6.75	0.822	0.334	0.145	2.071	<0.035	1.459	0.481	0.192	0.345i
2378-TetraBDF	6.50	18.6	3.91	3.88	0.117	<0.045	0.492	1.120	<0.01	0.572	0.106	0.204	0.113
12378-PentaBDF	9.11	15.12	5.43	5.22	<0.036	<0.063	0.105	1.213	<0.03	0.274	<0.056	<0.068	<0.157
23478-PentaBDF	9.62	27.32	8.87	7.09	<0.073	<0.081	0.114	1.651	<0.038	0.996	0.221	<0.053	<0.173
123478-HexaBDF	65.8	132.0	71.0	53.2	<0.13	0.132	1.176	10.154	<0.116	5.277	1.525	<0.148	ab
1234678-HeptabromoBDF	2161[bc]	4151[bc]	1624[c]	716.1	6.385	<0.132	9.738	269.85	<1.361	190.22	51.210	21.182	ab
TEQ [d] lower	40.28	77.92	32.17	17.97	0.143	0.091	0.334	5.029	<0.01	2.999	0.814	0.233	0.011
TEQ [d] upper	40.28	77.92	32.17	17.97	0.251	0.248	0.372	5.108	0.087	3.049	0.855	0.326	0.522
Sum	2303	4414	1746	796.0	1.13	289.4	11.92	7.93	22.04	53.84	1.73	0.053	1.22

[a], not measured; [b], significant interference from matrix, Hexa and Pentas not detected, but insignificant contribution from these to the Dioxin Equivalent TEF assumptions;
[c], indicative; [d], WHO$_{2005}$-TEQ calculated assuming the same toxicity TEF values for Dioxin TEQ
CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood

Table 10 Non-ortho polybrominated biphenyl (PBB) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	2	1	2	1	2	1	2		1	2	3	4
							ng kg^{-1} DS						
PBB-77	0.312	0.450	0.329	0.491	0.131	0.116	<0.04	0.176	<0.036	0.039[a]	<0.052	<0.048	0.064
PBB-126	0.204	0.133	0.346	0.370	<0.075	<0.082	<0.027	<0.079	<0.024	<0.039	<0.045	<0.041	<0.089
PBB-169	0.174	0.579	0.657	0.165	<0.076	<0.086	<0.038	<0.083	<0.034	<0.041	<0.047	<0.044	<0.231
TEQ[b] lower	0.022	0.019	0.042	0.039	<0.011	<0.011	<0.011	<0.011	<0.01	<0.011	<0.011	<0.011	<0.013
TEQ[b] upper	0.022	0.019	0.042	0.039	0.008	0.009	0.003	0.009	0.003	0.004	0.005	0.005	0.011
Sum	0.690	1.162	1.332	1.026	0.282	0.284	0.105	0.338	0.094	0.119	0.144	0.133	0.384

[a], indicative; [b] = WHO$_{2005}$-TEQ calculated assuming the same toxicity TEF values for PCB TEQ

CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood

Table 11 Ortho-polybrominated biphenyl (PBB) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	2	1	2	1	2	1	2		1	2	3	4
	μg kg⁻¹ DS												
BB-15	0.003	0.022	0.005	0.017	<0.002	<0.002	<0.002	<0.002	<0.002	0.026	0.004	<0.002	<0.003
BB-49	<0.002	<0.002	<0.003	<0.003	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.003
BB-52	<0.002	<0.002	<0.003	<0.003	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.003
BB-80	<0.002	<0.003	<0.003	<0.014	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.003
BB-101	<0.002	<0.002	<0.003	<0.003	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.003
BB-153	0.037	0.030	0.094	0.318	<0.002	<0.002	<0.002	<0.002	<0.002	0.004	0.002	<0.002	<0.003
Sum	0.05	0.06	0.11	0.36	0.01	0.01	0.01	0.01	0.01	0.04	0.01	0.01	0.02

CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood

Table 12 Mixed halogenated dibenzodiozin (PXDD) and dibenzofuran (PXDF) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	2	1	2	1	2	1	2		1	2	3	4
							ng kg^{-1} DS						
2Br78ClDf	0.559	1.361	1.277	0.738	0.120	0.229	<0.018	0.491	<0.079	0.341	0.194	<0.026	0.054
2Br78ClDx	0.981	0.426	0.140	0.169	0.044	0.135	<0.018	0.274	<0.078	0.052	0.030	<0.025	<0.021
2Br378ClDx	0.032	0.044	0.035	<0.022	<0.033	0.054	<0.014	0.127	<0.063	0.048	0.048	<0.021	0.019
23Br78ClDx	<0.023	<0.022	<0.027	<0.026	<0.021	<0.009	<0.009	0.015	<0.039	0.019	<0.013	<0.013	<0.011
1Br2378ClDx	<0.023	<0.022	<0.027	<0.027	<0.033	0.035	<0.014	0.056	<0.063	<0.028	0.051	<0.021	<0.017
2Br1378ClDx	<0.023	<0.022	<0.014	<0.014	<0.022	0.104	<0.009	0.180i	<0.041	<0.018	<0.014	<0.014	<0.011
2Br36789ClDx	0.046	0.211	0.035	0.113	0.162	0.380	<0.022	1.069	<0.101	<0.046	0.112	<0.033	0.027
3Br278ClDf	0.041	0.162	0.164	0.076	0.054	0.050	<0.014	0.212	<0.064	0.049	<0.021	<0.021	0.019
2Br678ClDf	0.115	0.180	0.181	0.118	0.073	0.090	0.007	0.195	<0.026	0.040	<0.009	<0.008	<0.007
23Br78ClDf	0.055	0.127	0.137	0.117	0.034	<0.007	<0.007	0.017	<0.028	<0.012	0.083	0.023	0.021
1Br2378ClDf	<0.023	<0.022	0.030	0.046	<0.021	<0.009	<0.009	<0.090	<0.04	<0.018	<0.013	<0.013	<0.011
4Br2378ClDf	0.092	0.149	0.298	0.141	0.257	0.076	<0.019	0.258	<0.087	0.084[a]	0.048[a]	0.052	<0.023
13Br278ClDf	<0.023	<0.022	0.034	<0.022	<0.009	0.012	<0.006	0.023	<0.018	<0.008	<0.006	<0.006	<0.007
Sum	2.036	2.771	2.400	1.629	0.883	1.190	0.166	3.005	0.727	0.763	0.642	0.276	0.248

[a] , indicative

CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood

Table 13 Mixed halogenated biphenyl (NXB) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	2	1	2	1	2	1	2		1	2	3	4
	ng kg^{-1} DS												
4'Br33'45Cl PXB 126	0.037	0.044	0.027	0.046	<0.060	<0.026	<0.026	0.034	<0.116	<0.052	0.045	<0.038	<0.031
34Br3'4'5'Cl PXB 126 di-Br	<0.023	<0.022	0.035	0.036	<0.014	<0.006	0.009	<0.006	<0.026	0.020	<0.008	<0.008	<0.007
3'4'5'Br34Cl PXB 126 tri-Br	<0.023	<0.022	<0.008	<0.008	<0.032	<0.014	<0.013	<0.014	<0.061	<0.027	<0.020	<0.019	<0.016
Sum	0.08	0.09	0.07	0.09	0.11	0.05	0.05	0.05	0.20	0.10	0.07	0.07	0.05

CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood

Table 14 Preliminary polycyclic aromatic hydrocarbon (PAH) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	2	1	2	1	2	1	2		1	2	3	4
						$\mu g\ kg^{-1}\ DS$							
benz (a) anthracene	19	87	23	22	0	5	4	21	<0.07	26	30	170	[a]
chrysene	69	153	116	97	0	8	5	27	<0.08	129	125	59	[a]
benzo[b]fluoranthene	169	302	107	270	0	4	5	25	<0.08	93	114	32	[a]
benzo[a]pyrene	157	176	90	174	0	6	4	23	<0.09	95	121	23	[a]
PAH 4 Sum Lower	414	719	336	563	1	23	17	97	<0.07	342	390	285	
PAH 4 Sum Upper	414	719	336	563	1	23	17	97	0	342	390	285	

Values reported to rounded figures are estimates only; [a],awaiting measurement

CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood

Table 15 Preliminary polybrominated diphenyl ether (PBDE) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**		**1**	**2**	**3**	**4**
	µg kg^{-1} DS												
BDE-17	0.688	0.856	0.688	0.409	0.003	0.005	89.7	0.005	<0.005	0.035	0.027	<0.002	0.007
BDE-28/33	0.745	0.609	1.940	1.368	0.005	0.009	<0.006	0.007	<0.006	0.047	0.032	0.011	0.008
BDE-47	32.85	25.39	12.927	10.388	0.077	0.088	<0.007	0.088	0.077	1.159	0.662	0.151	0.274
BDE-49	2.138	1.838	1.977	1.049	0.012	0.012	0.095	0.017	0.007	0.065	0.031	0.010	0.017
BDE-66	1.017	1.008	0.723	1.043	0.012	0.015	0.009	0.016	<0.007	0.063	0.028	0.010	0.017
BDE-71	0.317	0.453	0.141	0.117	<0.002	<0.002	0.008	<0.002	<0.002	0.006	<0.002	<0.002	<0.003
BDE-77	0.024	0.031	0.200	0.108	<0.002	<0.002	<0.002	<0.002	<0.002	0.004	<0.002	<0.002	<0.003
BDE-85	1.712	1.437	0.692	0.520	0.005	0.006	<0.002	0.006	<0.005	0.063	0.027	0.007	0.015
BDE-99	41.99	36.99	15.106	11.855	0.093	0.100	<0.006	0.115	<0.072	1.396	0.743	0.178	0.313
BDE-100	8.780	7.446	2.824	2.298	0.010	0.010	0.082	0.012	<0.009	0.271	0.145	0.032	0.056
BDE-119	0.115	0.226	0.330	0.125	<0.002	<0.002	0.012	0.003	<0.002	0.009	0.004	<0.002	<0.003
BDE-126	<0.024	<0.009	<0.015	<0.01	<0.002	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.003
BDE-153	5.308	5.79	7.225	2.779	0.018	0.014	<0.002	0.026	<0.006	0.333	0.137	0.032	0.047
BDE-138	0.593	0.438	0.691	0.286	0.002	<0.002	0.008	0.003	<0.002	0.028	0.012	<0.002	<0.003
BDE-154	3.977	3.930	2.253	1.406	0.009	<0.007	<0.002	0.014	0.003	0.138	0.074	0.016	0.031
BDE-183	2.945	4.074	19.027	6.694	0.006	0.005	0.007	0.008	<0.002	0.720	0.338	0.056	0.030
Sum	103.2	90.51	59.533	40.45	0.262	0.280	0.224	0.325	0.087	4.339	2.261	0.515	0.815
Sum 6[a]	87.8	76.8	58.5	34.5	0.21	0.22	0.20	0.26	0.17	3.79	1.99	0.45	0.70

[a] = 28, 47, 99, 153 154, 183

CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood

Table 16 Preliminary deca-brominated diphenyl ether (BDE)/brominated biphenyl (BB) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	2	1	2	1	2	1	2		1	2	3	4
	$\mu g\ kg^{-1}$ DS												
BDE-209	4198[a]	6693[a]	1723[a]	1650[a]	0.704	0.621	<0.172	3.014	1.350i	246.1	143.0	7.943	11.02
BB-209	0.067	0.288	0.479	0.146	0.020	0.029	<0.244	0.017	<0.218	0.180	0.009	0.009	0.15

[a], indicative out of linear range

CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood

Table 17 Hexabromocyclododecane (HBCD), pentabromocyclododecene and tetrabromobipshenol A (TBBPA) concentrations in the waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	2	1	2	1	2	1	2		1	2	3	4
	μg kg⁻¹ DS												
α-HBCD	8.3-19.7	9.05	26-70	121-302	<0.01	0.03[a]	0.12	<0.01	<0.01	19-45	9.35	0.76	1.06
ß-HBCD	5.5-9.6	6.37	3-7	34-78	<0.01	0.01[a]	0.03	<0.01	<0.01	10-20	4.31	0.22	0.31
γ-HBCD	302-390	391.74	4-25	139-836	<0.03	0.18[a]	<0.09	<0.02	<0.01	67-169	21.16	1.06	1.26
TBBPA	33-42.6	45.23	493-517	100.00	NM	<0.36[a]	42i	NM	NM	8.2-18.9	52[a]	0.19	1.37[a]
*PBCD	NM	7.07	13-29	42-351	<0.03	<0.09[a]	NM	<0.03	NM	2.7-9.0	0.82	<0.13	NM

[a], indicative value

Range values quoted where repeatability is varied due to sample heterogeneity

Table 18 Polychlorinated napthalene (PCN) concentrations in waste samples (DS basis)

	Biosolids		CLO		MBMA		PLA		PSA	RWW			
	1	2	1	2	1	2	1	2		1	2	3	4
	ng kg^{-1} DS												
PCN 52	209.1	120.6	379.3	123.6[a]	21.07	5.45	<1.84	37.58	<8.22	148.6[a]	103.74[a]	26.04	10.83
PCN 53	352.7	194.6	737.3	366.7[a]	12.19	<1.80	<1.78	3.70	<7.98	532.0[a]	347.79[a]	59.97	46.55
PCN 66/67	14.58	20.42	30.5	9.95	<1.4	2.94	<0.6	8.92	<2.69	12.58	6.99	1.18	0.87
PCN 68	31.04	31.01	107.0	30.59	<1.42	1.87	<0.6	5.64	<2.71	76.47	25.64	5.09	4.11
PCN 69	42.69	38.91	223.1	47.43	<1.80	<0.78	<0.77	1.55	<3.45	130.01	38.52	8.17	6.74
PCN 71/72	66.07	52.00	369.7	62.60	<2.08	<0.9	<0.89	<0.9	<3.99	203.0	55.06	15.31	14.21
PCN 73	12.79	39.35	40.1	18.76	<2.03	43.87	<0.87	1.69	<3.89	28.5	10.72	<1.27	<1.05
PCN 74	12.06	19.10	85.7	15.17	<1.49	20.65	<0.64	<0.64	<2.86	67.59	13.87	2.27	2.99
PCN 75	1.42	24.95	4.01	5.64	<1.87	29.62	0.80	<.81	<3.60	11.01	4.69	<1.18	<0.97
Sum PCN, lower	742.5	541.0	1976.7	680.4	33.26	104.4	<0.56	59.09	<2.7	1209.8	603.5	118.0	86.31
Sum PCN, upper	742.5	541.0	1976.6	680.4	45.35	107.9	8.80	61.45	39.42	1209.8	603.5	120.5	88.31

[a], indicative

CLO, compost-like-output; MBMA, meat and bone meal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood